Promoting the fast Na-storage and stable layered cathode for sodium-ion batteries by a site-selective substitution in triple crystallographic sites

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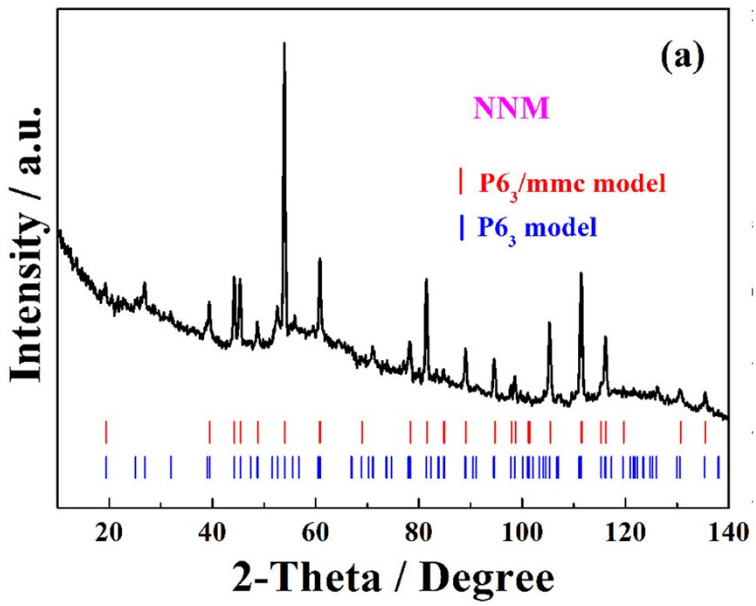

Figure S1 (a) Comparison of the neutron powder diffraction (NPD) data using $P6_3/mmc$ and $P6_3$ space groups.

Table S1 Refined crystal sites and atom occupancies of the NNM sample by XRD data. (Space group of $P6_3/mmc$)

Atom	Site	x	y	z
Na_1	2b	0	0	1/4
Na_2	2d	1/3	2/3	1/4
Mn	2a	0	0	0
Ni	2a	0	0	0
O	4f	1/3	2/3	0.09048

Table S2 Refined crystal sites and atom occupancies of the doped-NNM sample by XRD data. (Space group of $P6_3/mmc$)

Atom	Site	x	y	z
Na_1	2b	0	0	1/4
Ca_1	2b	0	0	1/4
Na_2	2d	1/3	2/3	1/4
Ca_2	2d	1/3	2/3	1/4
Mn	2a	0	0	0
Ni	2a	0	0	0
Li	2a	0	0	0
O	4f	1/3	1/3	0.09091
F	4f	1/3	1/3	0.09091

Table S3 Refined crystal sites and atom occupancies of the NNM sample by NPD data using super cell model. (Space group of $P6_3$, $R_p\%$ = 2.22, $R_{wp}\%$ = 3.00)

Atom	Site	x	y	z
Na_1	2a	0	0	1/4
Na_2	6c	1/3	0	1/4
Na_3	2b	1/3	2/3	1/4
Na_4	2b	2/3	1/3	1/4
Mn_1 / Ni_1	2a	0	0	0
Mn_2 / Ni_2	2b	1/3	2/3	1/2
Mn_3/ Ni_3	2b	1/3	2/3	0
O_1	6c	0.3383	0.0059	-0.4303
O_2	6c	0.6545	0.0259	0.3882

Table S4 Refined crystal sites and atom occupancies of the doped-NNM sample by NPD data using super cell model. (Space group of $P6_3$, R_p% = 2.71, R_{wp}% = 3.69)

Atom	Site	x	y	z
Na_1	2a	0	0	1/4
Na_2	6c	1/3	0	1/4
Ca	6c	1/3	0	1/4
Na_3	2b	1/3	2/3	1/4
Na_4	2b	2/3	1/3	1/4
$Mn_1/Ni_1/Li_1$	2a	0	0	0
$Mn_2/Ni_1/Li_1$	2b	1/3	2/3	1/2
$Mn_3/Ni_1/Li_1$	2b	1/3	2/3	0
O_1/F_1	6c	0.3814	0.0276	-0.3800
O_2/F_2	6c	0.6702	0.0090	0.4399

Table S5 Refined lattice parameters of all the materials based on XRD data.

Sample	a = b (Å)	c (Å)	Factors (%)
NNM	2.8923	11.1739	R_p = 4.79, R_{wp} = 6.63, $\chi2$ = 2.43
Doped-NNM	2.8848	11.0496	R_p = 4.39, R_{wp} = 5.93, $\chi2$ = 2.14
Ca-NNM	2.8888	11.1609	R_p = 4.82, R_{wp} = 6.51, $\chi2$ = 2.28
Li-NNM	2.8870	11.0374	R_p = 4.48, R_{wp} = 6.10, $\chi2$ = 2.44

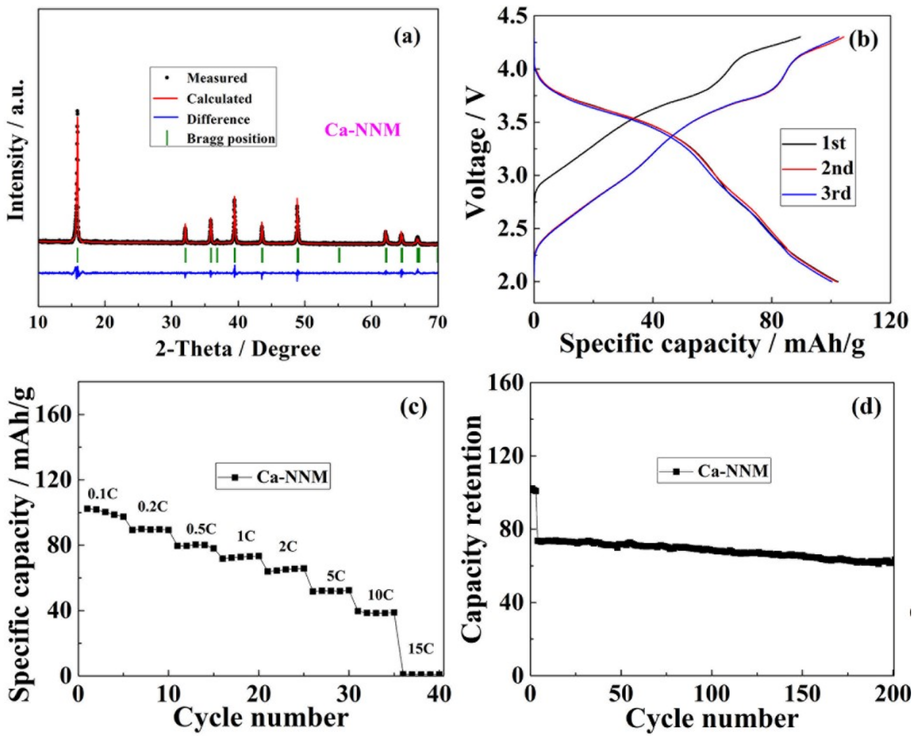

Figure S2 (a) XRD plot of single Ca-doped cathode material (Ca-NNM), (b) Initial charge/discharge profiles, (c) Rate capability and (d) Cycling performance of Ca-NNM cathode at 1C in the voltage of 2.0 - 4.3 V.

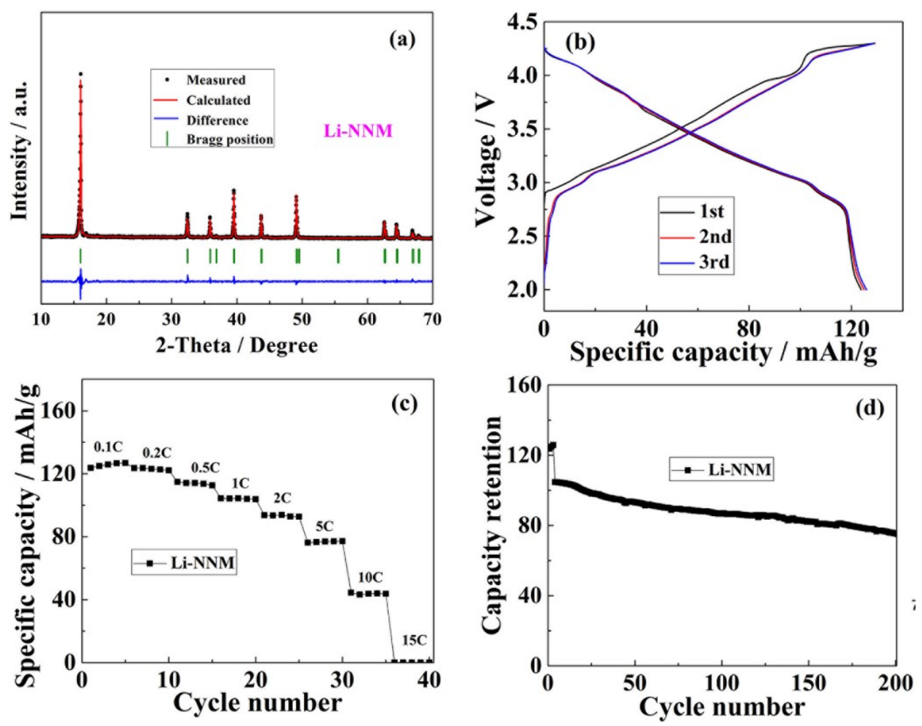

Figure S3 (a) XRD plot of single Li-doped cathode material (Li-NNM), (b) Initial charge/discharge profiles, (c) Rate capability and (d) Cycling performance of Li-NNM cathode at 1C in the voltage of 2.0 - 4.3 V.

Table S6 Comparison of electrochemical performance of all the as-prepared cathode materials.

Sample	Specific capacity (mAh g^{-1})								Cycling Stability
	0.1 C	0.2C	0.5C	1C	2C	5C	10C	15C	
NNM	166	126	93	79	58	28	0	0	20/79 = 25.3%
Doped-NNM	117	114	109	104	99	89	76	64	91/104= 87.5%
Ca-NNM	102	90	79	73	65	51	38	0	62/73= 84.9%
Li-NNM	125	123	113	104	93	76	45	0	74/104= 71.1%

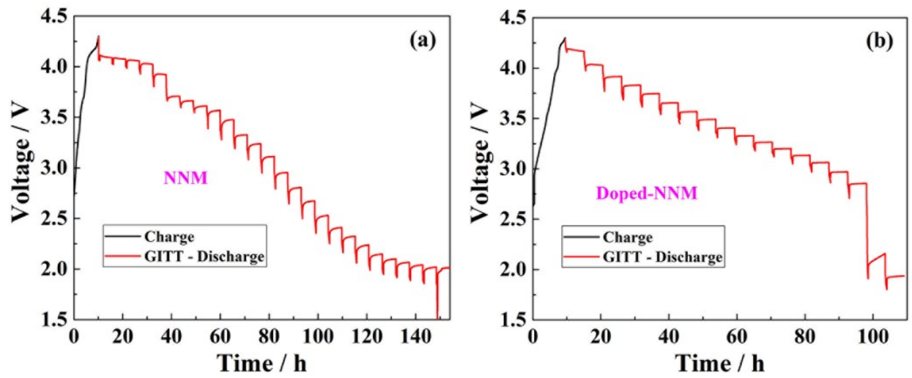

Figure S4 GITT plots of (a) NNM and (b) doped-NNM cathodes upon discharging at 0.1 C in the voltage range of 2.0 - 4.3 V.

The calculated Na-ion diffusion coefficient by the Galvanostatic intermittent titration (GITT) equation:

$$D_{Na} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad \text{(S1)}$$

Where m_B, M_B and V_M correspond to the electrode mass, molecular weight and molar volume of the as-prepared materials; S is the surface area (0.785 cm^2), which is calculated from the geometrical area in this work. τ (s) is the testing time in each step. ΔE_s and ΔE_τ represent the quasi-equilibrium potential and the change of voltage E during the current pulse, respectively.[1-5]

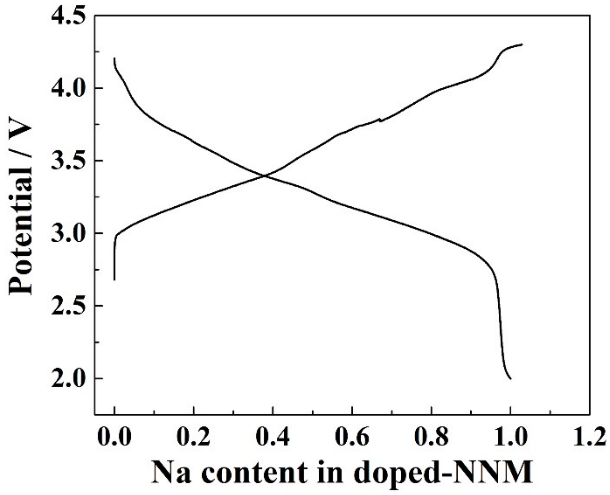

Figure S5 Normalized charge and discharge profiles of doped-NNM cathode during the in situ XRD experiments.

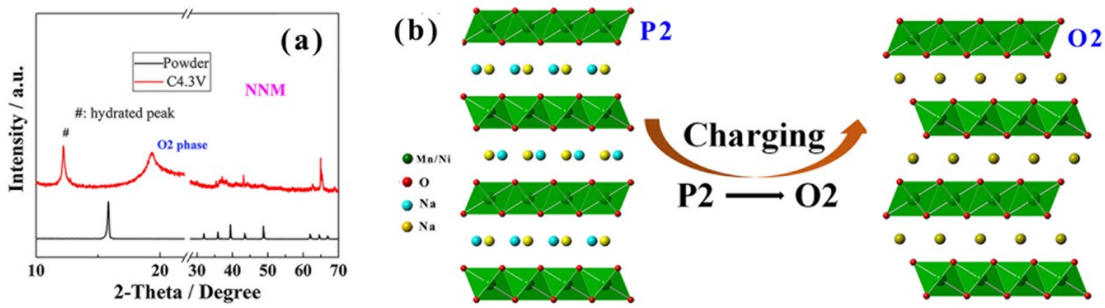

Figure S6 (a) Ex situ XRD data of undoped NMM cathode, (b) illustration of structural evolution of the pristine NNM cathode.

REFERENCES

1 K. Liu, S. S. Tan, J. Moon, C. J. Jafta, C. Li, T. Kobayashi, H. Lyu, C. A. Bridges, S. Men, W. Guo, Y. F. Sun, J. L. Zhang, M. P. Paranthaman, X. G. Sun and S. Dai, *Adv. Energy Mater.*, 2020, **10**, 2000135.

2 J. Jin, Y. Liu, Q. Shen, X. Zhao, J. Zhang, Y. Song, T. Li, X. Xing and J. Chen, *Adv. Funct. Mater.*, 2022, **32**, 2203424.

3 C. Zhao, F. Ding, Y. Lu, L. Chen and Y.-S. Hu, *Angew. Chem.-Int. Edit.*, 2020, **59**, 264-269.

4 P. Zou, L. Yao, C. Wang, S. J. Lee, T. Li and H. L. Xin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202304628.

5 H. Fang, H. Ji, J. Zhai, C. Wang, C. Zhu, G. Chen, M. Chu, T. Zhang, Z. Ma, W. Zhao, W. Ji and Y. Xiao, *Small*, 2023, **19**, 2301360.